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NOTES

Atom Transfer Radical Polymerization of Methyl Methacrylate under Microwave Irradiation

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Atom transfer radical polymerization (ATRP) has been expanding continuously.[1–3] However, a large amount of catalyst, long reaction time and a high temperature are ordinarily needed in ATRP for gaining a higher polymerization rate. To solve the problem, a new catalyst system with higher reactivity or additional measures to enhance the reactivity of present catalyst system is needed. Microwave, as peculiar source of energy, has been widely applied to enhance chemical reaction.[4–6] The main benefits of performing reactions under microwave irradiation (MI) are the significant rate-enhancements, namely, it can enhance reactivity of reaction system. In addition, Klumperman *et al.*[7] reported that copper(I) thiocyanate (CuSCN) was able to induce faster polymerization of MMA compared to CuCl or CuBr. So this paper reports the ATRP of MMA with a CuSCN-based catalyst system under microwave irradiation. The main purpose of this work is to enhance the polymerization rate, decrease the dosage of the catalyst with the help of microwave irradiation.

EXPERIMENTAL

Experimental Apparatus

Irradiation power of the self-improved domestic microwave oven (M9D88 SANSUNG) is from 90 W to 900 W. The reactor is a two-neck bottle (500 mL) with refluxing solvent (400 mL, carbon tetrachloride, dielectric constant 2.238) used for controlling the reaction temperature (81 °C), Which is slightly higher than boiling point of the solvent (76.8 °C). The dry sealed glass tube filled with reaction materials was placed into the refluxing solvent to let polymerization take place.

Materials

Methyl methacrylate (MMA) (Chemically Pure, Shanghai Chemical Reagent Co., LTD.) was purified by extracting with 5% sodium hydroxide aqueous solution, followed by washing with water and dried with sodium sulfate anhydrous overnight, finally distillated under vacuum. *N*,*N*,*N*′,*N*′,*N*′′-pentamethyldiethylenetriamine (Chemically Pure, Jiangsu Liyang Jiangdian Chemical Factory) was dried with 4 Å molecular sieve and distillated under vacuum. *p*-Toluene sulfonyl chloride (*p*-TsCl) (Chemically Pure, Shanghai Chemical Reagent Co., LTD.) was recrystalyzed with petroleum ether. Copper(I) thiocyanate (CuSCN) (98.04% Yixing Liaoyuan Chemical Co., LTD.) was purified by washing with acetic acid and acetone, then dried under vacuum. Tetrahydrofuran (THF) (Analytical Reagent, Shanghai Chemical Reagent Co., LTD.), hydrochloric acid (HCl) (Analytical Reagent, Jiangsu Jincheng Chemical Reagent Co., LTD.), and methanol (commercially available) were used as received.

Polymerization

Microwave Irradiation (MI) Process. A dry glass tube was filled with MMA, *p*-TsCl, CuSCN and PMDETA. Three freeze-pump-thaw cycles were performed, and the tube was sealed under vacuum and placed into the self-improved microwave oven with reflux of carbon tetrachloride (81 °C). The polymerization was stopped at a desired time by cooling the tubes into ice water. Afterwards, the tube was opened and contents were dissolved in THF, precipitated into a large amount of methanol/HCl (100/0.05, volume ratio). The dried product was then characterized by gravimetry.

Conventional Heating (CH) Process. The sealed tube under vacuum was placed in an oil bath held by a thermostat at the desired temperature to polymerize.

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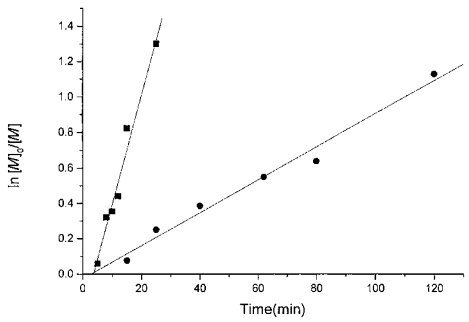

Figure 1. Kinetics of ATRP of MMA under MI and CH $[MMA]_0$ = 9.46 M; Microwave Power = 450 W $[MMA]_0$: $[p\text{-TsCl}]_0$: $[CuSCN]_0$: $[PMDETA]_0$ = 500:1:1:3 (■: MI(81°C); ●: CH(81°C)).

The other procedures were identical to that under MI.

Measurements

Conversion of monomer was determined by gravimetry. Molecular weights and molecular weight distributions were measured using Waters 1515 GPC with THF as a mobile phase and with column temperature of 30 °C. Polystyrene standards were used to calibrate the columns.

The concentration of Cu in the solution of MMA/CuSCN/PMDETA was determined by HITACHI 180-80 Polarized Zeeman atomic absorption spectrophotometers.

RESULTS AND DISCUSSION

Polymerization in bulk catalyzed by CuSCN/PMDETA appeared to be heterogeneous. Figure 1 shows the kinetic plot of ln ($[M]_0/[M]$) *vs.* time for ATRP of MMA using different polymerization processes (MI and CH). The resulting slopes indicate the polymerizations proceeded with an approximately constant number of active species for the duration of the reaction. According to the slopes of the kinetics, the apparent rate constant, k_p^{app}, was calculated. k_p^{app} under MI(81 °C : 1.063×10^{-3} s^{-1}) is much higher than that under CH(81 °C : 1.56×10^{-4} s^{-1}), which indicates that applying MI can dramatically enhance the rate of polymerization compare to CH. Whether under CH or MI, the induction period can be seen, a similar phenomenon has been observed by Klumperman *et al.*[8]

Figure 2 shows the molecular weight, $M_{n(GPC)}$, and molecular weight distribution, M_w/M_n, as a function of conversion. $M_{n(GPC)}$ increased with increasing of conversion, the $M_{n(GPC)}$closes to the calculated $M_{n,th}$, indicating that a relatively high initiating efficiency. At lower conversion(< 50%), the polydispersities under MI(about 1.15) are slightly narrower than those under CH(about 1.2), however, the polydispersities

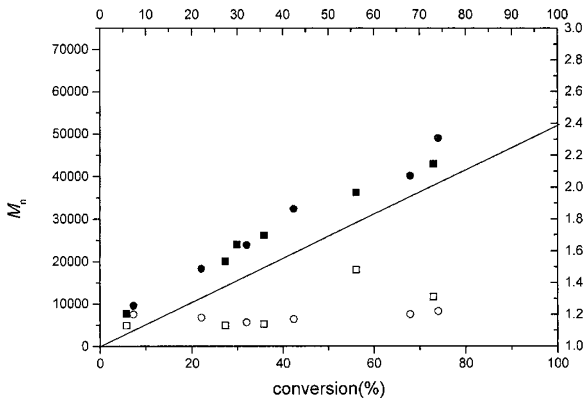

Figure 2. Dependence of $M_{n(GPC)}$ and M_w/M_n on Conversion in ATRP of MMA under MI and CH at 81°C. Microwave Power = 450 W. $[MMA]_0$ = 9.46 M; $[MMA]_0$:$[p\text{-TsCl}]_0$:$[CuSCN]_0$:$[PMDETA]_0$ = 500:1:1:3 [■:M_n(MI); ●(CH) □: M_w/M_n(MI)] ○:M_w/M_n(CH) —:$M_{n,th}$.

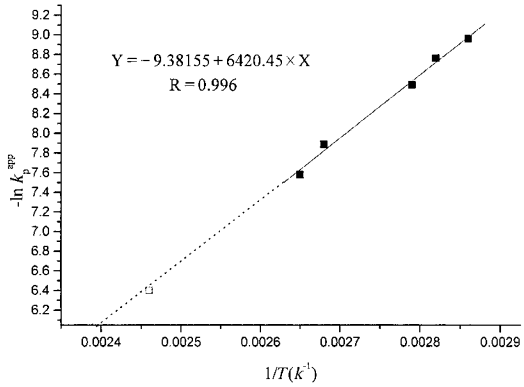

Figure 3. Plots of $-\ln K_p^{app}$ *vs.* 1/T for ATRP of MMA under CH ■: exp. □:th.

under MI(about 1.35) are bordener than those under CH(about 1.2) at higher conversion, which may be due to more side reactions taking place.

The Arrhenius plot for the CuSCN/PMDETA catalyzed polymerization of MMA is shown in Figure 3, as mentioned above that the k_p^{app} at 81 °C under MI is 1.063×10^{-3} s^{-1}, according to the plots shown in Figure 3, a polymerization temperature of 134°C under CH will be needed to reach the same polymerization rate, indicating the temperature difference under MI and CH should be 53 °C, which is much higher than the actual temperature difference. This difference may ascribe to non-thermal effect.[9] In order to further investigate the non-thermal microwave effect, the concentration of Cu in the solution of this heterogonous system was determined; the results (Figure 4) show that the concentration of Cu under MI is higher than that under CH within the same time. So applying MI to polymerization can enhance the rate of polymerization.

As shown in Figure 5 that the rate of polymerization follows first order with respect to the concentration of the Cu (I) catalyst in the limited range. ([CuSCN] <

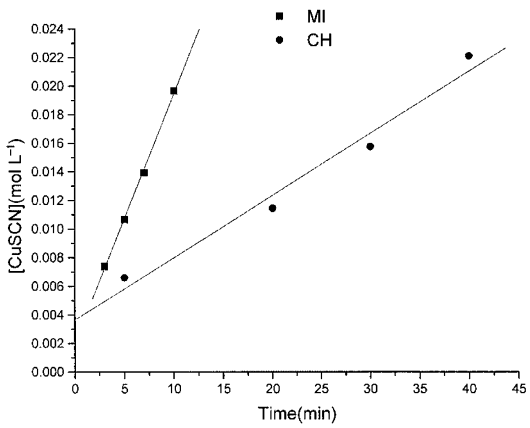

Figure 4. Plot of [Cu] *vs.* Time in the solution of MMA/CuSCN/PMDETA. [MMA]:[CuSCN]:[PMDETA] = 1000:0.5:1.5, [CuSCN] = 0.00484 mol L^{-1}, ■: MI;. ●:CH.

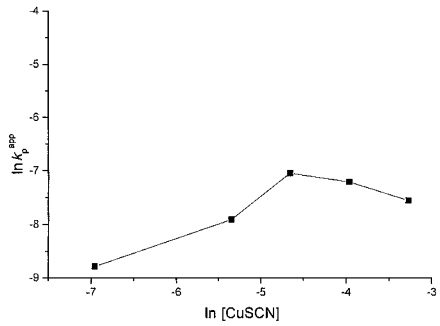

Figure 5. Dependence of K_p^{app} on the catalyst concentration for ATRP of MMA in bulk at 81°C under MI. $[MMA]_0$ = 9.46M; $[p\text{-TsCl}]_0$ = 0.0946 M $[CuSCN]_0/[PMDETA]_0$ = 1:3.

0.0095 mol L^{-1}.), this is agree with the case when CuCl and CuBr is used as the catalyst of ATRP of MMA under CH.[10] The apparent rate constant is approximately independent of [CuSCN] when the concentrations of CuSCN surpass 0.0095 mol L^{-1}. Obviously, the concentration of CuSCN is a key parameter here. Indeed, CuSCN has reached the saturated concentration in the solution under MI. Exceed CuSCN cannot play a role during polymerization. A small amount of CuSCN (0.00095 mol L^{-1}.) can also effectively catalyze the ATRP of MMA under MI. So applying microwave irradiation can dramatically reduce the dosage of CuSCN, which also prove the existence of non-thermal effect under MI.

CONCLUSION

MMA *via* ATRP can be successfully carried out using *p*-TsCl/CuSCN/PMDETA as the catalyst system under microwave irradiation. Well-controlled polymerization of MMA with narrow polydispersities (1.1~1.5) have been achieved. Applying MI to the ATRP of MMA can significantly enhanced the rate of polymerization. Plots of ln $([M]_0/[M])$ *vs.* time and molecular weight *vs.* conversion show a linear dependence. Applying microwave irradiation can dramatically reduce the dosage of catalyst in ATRP.

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